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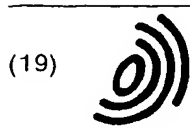
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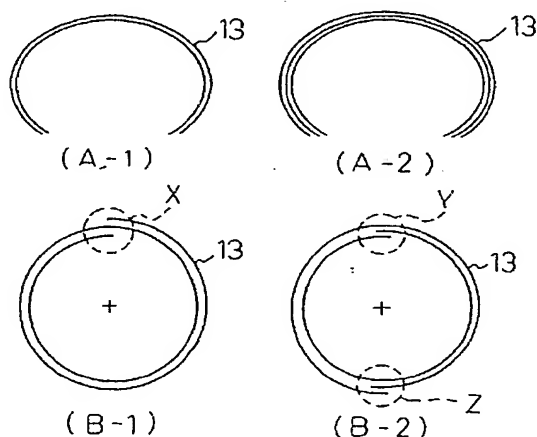
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(54) Pneumatic tire

(57) A pneumatic tire having at least one air permeation preventive layer comprised of a cylindrical film or sheet extruded, molded or heat-fused into a cylindrical shape and free from any connecting portion, composed of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and an elastomer component and having an air permeation coefficient of not more than $25 \times 10^{-12} \text{cc-cm/cm}^2\text{-sec-cmHg}$ and a Young's modulus of 1 to 500MPa, wherein a plurality of air permeation preventive layers cover the inner surface of the tire by at least two continuous turns substantially in the tire circumferential direction.

Fig. 5



Description

TECHNICAL FIELD

5 [0001] The present invention relates to a pneumatic tire, more particularly it relates to a lightweight pneumatic tire having a structure which can be manufactured with a good productivity without detracting from the resistance to air leakage, uniformity, rolling resistance, durability, etc.

BACKGROUND ART

10 [0002] Reduction of fuel consumption is one of the major technical issues in automobiles. As one of the means for this issue, demands for reduction of the weight of pneumatic tires have been strongly increased. On the other hand, an inner liner layer or other air permeation preventive layer comprised of a halogenated butyl rubber or other rubber having a low air permeability is conventionally provided at the inner surface of the pneumatic tire to maintain a constant
15 tire air pressure.

[0003] However, a halogenated butyl rubber has a large hysteresis loss, and therefore, after vulcanization of the tire, when rippling is caused in the rubber of the inner surface of the carcass layer and the inner liner layer, since the inner liner layer deforms along with deformation of the carcass layer, there is the problem of an increase of the rolling resistance. Therefore, in general, a rubber sheet called a "tie rubber" having a small hysteresis loss has been inserted
20 between the inner liner layer (for example, halogenated butyl rubber) and rubber of the inner surface of the carcass layer when joining the two. Accordingly, in addition to the thickness of the inner liner layer of the halogenated butyl rubber, the thickness of the tie rubber is added and the layer overall becomes a thickness of over 1 mm (i.e., 1,000 μm). As a result, this has become a factor increasing the weight of the final tire.

[0004] Techniques have been proposed for using various materials in place of the butyl rubber or other low air permeability rubber as the inner liner layer of a pneumatic tire. For example, Japanese Examined Patent Publication (Kokoku) No. 47-31761 discloses to coat the inner surface of a vulcanized tire with, at a thickness of not more than 0.1 mm, a solution or dispersion of a synthetic resin such as a polyvinylidene chloride, saturated polyester resin, or polyamide resin having an air permeation coefficient [cm^3 (standard state)/ $\text{cm}\cdot\text{sec}\cdot\text{mmHg}$] of not more than 10×10^{-13}
25 at 30°C and not more than 50×10^{-13} at 70°C.

[0005] Japanese Unexamined Patent Publication (Kokai) No. 5-330307 discloses to halogenate the inner surface of the tire (using a conventionally known chlorination solution, bromine solution, or iodine solution) and form, on the top thereof, a polymer film (the thickness = 10 to 200 μm) of methoxymethylated nylon, copolymer nylon, a blend of polyurethane and polyvinylidene chloride, or a blend of polyurethane and polyvinylidene fluoride.

[0006] Further, Japanese Unexamined Patent Publication (Kokai) No. 5-318618 discloses a pneumatic tire using a
35 thin film of methoxymethylated nylon as an inner liner. According to this technique, a solution or emulsion of methoxymethylated nylon is spread or coated on the inner surface of a green tire, then the tire is vulcanized or a solution or emulsion of methoxymethylated nylon is spread or coated on the inner surface of the tire after vulcanization so as to produce the pneumatic tire.

[0007] Further, Japanese Unexamined Patent Publication (Kokai) No. 6-40207 is an example of using as an air permeation preventive layer composed of a tire a multilayer film having a low air permeability layer comprised of a polyvinylidene chloride film or ethylenevinyl alcohol copolymer film and an adhesive layer comprised of a polyolefin film, aliphatic polyamide film, or polyurethane film. In this example, it is proposed to laminate the low air permeability layer and the adhesive layer to form a thin film and to laminate that thin film on the inner surface of a green tire comprised of unvulcanized rubber so that the adhesive layer contacts the carcass layer, then vulcanize and mold the green tire
40 so as to provide an air permeation preventive layer on the inside of the tire. By using this multilayer film as the air permeation preventive layer, it is possible to reduce the thickness of the air permeation preventive layer from the past and to reduce the weight of the tire without detracting from the retention of the air pressure. However, when forming an air permeation preventive layer such as the inner liner from such a thermoplastic multilayer film, if the bond at the connecting portion (i.e., splice portion) of the multilayer film becomes poor, the splice portion of the liner of the final product may end up opening. Further, since the elongation of the splice portion is small at the time of inflation in the process for molding the tire, the uniformity of the tire is decreased and there is the possibility of occurrence of vibration when the automobile is being driven or a decline in the high speed durability.

[0008] Japanese Unexamined Patent Publication (Kokai) No. 59-93344 discloses an apparatus for forming a tire by adhering a cylindrical member of an inner liner etc. to the inside of a green tire. According to this apparatus, the cylindrical inner liner (i.e., cylindrical member) is continuously extruded from an extruder, inserted into the green tire carried on the tire table, and made to adhere to the inside of the green tire by inflation of a bladder. However, if it is attempted to use this apparatus when using a thermoplastic film as the inner liner material, when extruding the cylindrical film continuously downward, since the thermoplasticity is large, the cylindrical shape will not be held or the
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precision of the thickness of the film will not be obtained and the problem will arise of difficulty in cutting the cylindrical member (that is, the cylindrical thermoplastic film) inserted into the green tire by a cutter.

[0009] As explained above, various materials have been proposed for making the inner liner layer of a pneumatic tire in place of butyl rubber, but none has yet been commercialized. In view of this situation, we previously proposed, as a new material for an air permeation preventive layer, a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and elastomer having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa (for example, see specifications of Japanese Patent Application Nos. 7-150353, 7-28318, 7-28257, 7-26844, 7-28320, 7-11752, etc.)

[0010] However, when fabricating an air permeation preventive layer, for example, as shown in Figs. 1(a) and (b), in the case of the conventional butyl rubber liner, when moving from the first molding step to the second molding step at the time of processing, the lift caused in the second molding step shown in Fig. 1(b) causes the connecting portion 3 of the film liner 2 at the bottom of the carcass layer 1 to elongate, and therefore, makes the tack of the film liner smaller, and therefore, the splice portion of the film liner ends up opening up (i.e., splice opening 4).

[0011] Further, as shown in Fig. 2, in a tire of a conventional single-ply carcass structure comprised of a carcass 5, inner liner layer (air permeation preventive layer) 6, and tie rubber 7, there is the problem of the occurrence of an air deposit A caused by the step difference of the splice portion (connecting portion) 8. To avoid this, the splice portion 8' of the inner liner layer 6/tie rubber 7 and splice portion 8'' of the carcass 5 are offset in the circumferential direction as shown in Fig. 3 so as to keep the step difference of the splice portions small during the molding. However, with this molding method, there is a major problem in the productivity of the tire.

DISCLOSURE OF INVENTION

[0012] Accordingly, in view of the problems in the conventional pneumatic tires using a thermoplastic film for the air permeation preventive layer that, as explained above, when the bond of the connecting portion (i.e., splice portion) of the film in the tire manufacturing process is not sufficient, the connecting portion will open up at the time of inflation and cause a defective tire to be produced or that, since the elongation of the film connecting portion is smaller than other portions of the film, the air permeation preventive layer as a whole will not stretch uniformly at the time of inflation in the tire molding process and, therefore, problems will occur in the uniformity of the tire or the splicing work of the connecting portions of the film will become complicated, the object of the present invention is to solve the above problems and provide a pneumatic tire with a good work efficiency which enables a reduction of weight of the tire, has a uniform elongation of the air permeation preventive layer as a whole at the time of inflation without detracting from the retention of the air pressure in the tire, and further is free from the connecting portion opening at the time of molding the tire and causing the production of a defective tire as in the past.

[0013] In accordance with the present invention, there is provided a pneumatic tire comprising an air permeation preventive layer comprised of a film or sheet composed of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and an elastomer having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa wherein the film or sheet is arranged in such a manner that at least one turn of the film or sheet in the tire circumferential direction is free from a join.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The present invention will now be explained in further detail with reference to the drawings.

[0015] Figure 1 is a view explaining the problem of splice opening of a film liner in the conventional molding of a tire.

[0016] Figure 2 is a conceptual sectional view of the phenomenon of an air deposit at a splice portion between the carcass and inner liner in a single-ply carcass structure of a conventional pneumatic tire.

[0017] Figure 3 is a sectional conceptual view of the typical structure of a splice portion of a carcass, inner liner, and tie rubber of a conventional single-ply carcass structure.

[0018] Figure 4 is a semi-sectional view in the meridial direction of the construction of an inner liner portion of a pneumatic tire of the present invention.

[0019] Figure 5 are views of the arrangement of the polymer film of the air permeation preventive layer according to the present invention at a tire section and sides and shows in Fig. (A-1), (A-2), (B-1), and (B-2) several states of the same.

[0020] Figure 6 is a view explaining the requirement of uniformity of a polymer film for an air permeation preventive layer according to the present invention.

[0021] Figure 7 is a view explaining why the problem of splice opening does not occur in the air permeation preventive layer according to the present invention.

[0022] Figure 8 is a conceptual sectional view of a structure of a splice portion obtained by use of a film having a low air permeability compared with butyl rubber to laminate the air permeation preventive layer and carcass in advance

and simultaneously splice the same.

[0023] Figure 9 is a conceptual sectional view of the structure of a splice portion according to a first embodiment of a third aspect of the present invention.

[0024] Figure 10 is a conceptual sectional view of the structure of a splice portion according to a second embodiment of the third aspect of the present invention.

[0025] Figure 11 is a conceptual sectional view of the structure of a splice portion according to a third embodiment of the third aspect of the present invention.

[0026] Figure 12 is a conceptual sectional view of the structure of a splice portion according to an embodiment of a fourth aspect of the present invention.

[0027] The configuration, mode of operation, and effects of the present invention will be explained in further detail below.

[0028] As the air permeation preventive layer of the pneumatic tire according to the present invention, a film composed of a thermoplastic elastomer composition comprised of a thermoplastic resin or a thermoplastic resin and an elastomer component having a lower air permeability than the conventional butyl rubber is used. The film has an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg, preferably not more than 5×10^{-12} cc-cm/cm²-sec-cmHg, and a Young's modulus of 1 to 500 MPa, preferably 10 to 300 MPa. Further, the thickness of the film is preferably 0.02 to 0.2 mm, more preferably 0.05 to 0.2 mm. If the air permeation coefficient exceeds 25×10^{-12} cc-cm/cm²-sec-cmHg, the air permeation preventive layer must be made thicker in order to hold the tire air pressure, and therefore, this is not preferred from the viewpoint of lightening the weight of the pneumatic tire. Further, if the Young's modulus is too low, the moldability is reduced due to the occurrence of wrinkles and elongation at the time of molding the tire, while conversely if too high, there are problems in the durability.

[0029] The thermoplastic resin may be made any material having an action preventing permeation of air. Examples of such a thermoplastic resin are the following thermoplastic resins and any polymer mixtures of these thermoplastic resin components or these thermoplastic resin components and elastomer components etc.

[0030] As the thermoplastic resin, polyamide resins (for example, nylon 6 (N6), nylon 66 (N66), nylon 46 (N46), nylon 11 (N11), nylon 12 (N12), nylon 610 (N610), nylon 612 (N612), nylon 6/66 copolymer (N6/N66), nylon 6/66/610 copolymer (N6/66/610), nylon MXD (MXD6), nylon 6T, nylon 6/6T copolymer, nylon 66/PP copolymer, and nylon 66/PPS copolymer) and N-alkoxyalkylates of these, for example, methoxymethylates of 6-nylon, methoxymethylates of 6-610-nylon, and methoxymethylates of 612-nylon, polyester resins (for example, polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyethylene isophthalate (PEI), PET/PEI copolymers, polyacrylate (PAR), polybutylene naphthalate (PBN), liquid crystal polyester, polyoxyalkylene diimid diacid/polybutyrate terephthalate copolymer, and other aromatic polyesters), polynitrile resins (for example, polyacrylonitrile (PAN), polymethacrylonitrile, acrylonitrile/styrene copolymer (AS), methacrylonitrile/styrene copolymers, methacrylonitrile/styrene/butadiene copolymers, polymethacrylate resins (for example, polymethyl methacrylate (PMMA), polyethyl methacrylate), polyvinyl resins (for example, vinyl acetate, polyvinyl alcohol (PVA), vinyl alcohol/ethylene copolymer (EVOH), polyvinylidene chloride (PD-VC), polyvinyl chloride (PVC), polyvinyl/polyvinylidene chloride copolymer, polyvinylidene chloride/methyl acrylate copolymer, vinylidene chloride/acrylonitrile copolymer), cellulose resins (for example, cellulose acetate, cellulose acetobutyrate), fluororesins (for example, polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), polychlorofluoroethylene (PCTFE), tetrafluoroethylene/ethylene copolymer), imide resins (for example, aromatic polyimides (PI)), etc. may be exemplified.

[0031] The elastomer component which may be blended with the above thermoplastic resin is not particularly limited in type or amount so long as it forms a composition in the state blended with the thermoplastic resin component which, as a result, has the above air permeation coefficient and Young's modulus. Examples of such an elastomer are as follows.

[0032] Diene rubbers and the hydrogenated products thereof (for example, NR, IR, epoxylated natural rubber, SBR, BR (high cis-BR and low-cis BR), NBR, hydrogenated NBR, hydrogenated SBR), olefin rubbers (for example, ethylene propylene rubber (EPDM, EPM), maleic acid-modified ethylene propylene rubber (M-EPM), IIR, isobutylene and aromatic vinyl or diene monomer copolymers, acryl rubbers (ACM), ionomers), halogenated rubbers (for example, Br-IIR, Cl-IIR, bromide of isobutylene paramethylstyrene copolymer (Br-IPMS), CR, chlorohydrin rubber (CHR), chlorosulfonated polyethylene (CSM), chlorinated polyethylene (CM), maleic acid-modified chlorinated polyethylene (M-CM), silicone rubbers (for example, methylvinyl silicone rubber, dimethyl silicone rubber, methylphenylvinyl silicone rubber), sulfur-containing rubber (for example, polysulfide rubber), fluororubber (for example, vinylidene fluoride rubber, fluorine-containing vinyl ether rubber, tetrafluoroethylene propylene rubber, fluorine-containing silicone rubber, fluorine-containing phosphazene rubber), thermoplastic elastomers (for example, styrene elastomers, olefin elastomers, ester elastomers, urethane elastomers, polyamide elastomers), etc. may be exemplified.

[0033] The method for producing the thermoplastic elastomer composition constituting the air permeation preventive layer in the present invention consists of melting and kneading the thermoplastic resin component and elastomer component (in the case of rubber, the unvulcanized rubber) in advance by a biaxial kneader/extruder etc. to disperse

the elastomer component in the thermoplastic resin forming the continuous phase. When vulcanizing the elastomer component, a vulcanization agent is added, while kneading, and the elastomer component is dynamically vulcanized. Further, the various compounding agents (except vulcanization agent) for the thermoplastic resin or elastomer component may be added during the above kneading, but preferably are mixed in advance before the kneading. The kneader used for kneading the thermoplastic resin and the elastomer component is not particularly limited. Examples thereof are a screw extruder, kneader, Banbury mixer, biaxial kneader/extruder, etc. Among these, it is preferable to use a biaxial kneader/extruder for the kneading of the thermoplastic resin and the elastomer and the dynamic vulcanization of the elastomer component. Further, two or more types of kneaders may be used for successive kneading. As the conditions for the melting and kneading, the temperature should be at least the temperature where the thermoplastic resin melts. Further, the shear rate at the time of kneading is preferably 1000 to 7500 sec⁻¹. The time for the overall kneading is from 30 seconds to 10 minutes. Further, when adding a vulcanization agent, the vulcanization time after addition is preferably 15 seconds to 5 minutes. The polymer composition produced by the above method is then extruded or calendered into a film. The method of forming the film may be a usual method of forming a film from a thermoplastic resin or thermoplastic elastomer.

[0034] The thin film obtained in this way takes the structure of a matrix of the thermoplastic resin (A) into which the elastomer component (B) is dispersed as a discontinuous phase. By adopting such a state of dispersion, it is possible to impart a balance of pliability and resistance to air permeation and further possible to obtain the effect of improvement of the resistance to heat deformation, improvement of the waterproofness, etc. Also, thermoplastic processing becomes possible. Therefore, it becomes possible to form a film by an ordinary plastic molding machine, that is, by extrusion molding or calendering. The method for forming a film may be any method usable for forming a film from an ordinary thermoplastic resin or thermoplastic elastomer. Further, the bonding between the film and the opposing rubber layer may be achieved by using a usual chlorinated rubber, phenolic resin, or isocyanate adhesive and using the heat and pressure at the time of vulcanization and molding. These adhesives may be, for example, a phenolic resin (Chemlock 220), chlorinated rubber (Chemlock 205), isocyanate (Chemlock 402), etc.

[0035] When the compatibilities of specific thermoplastic resins and elastomer components differ, it is possible to make the both components compatible using a suitable compatibilizer as a third component. By mixing a compatibilizer into the system, the surface tension of the thermoplastic resin and elastomer component falls and as a result the size of the rubber particles forming the dispersion layer become finer, and therefore, the characteristics of the two components becomes more effectively expressed. As such a compatibilizer, in general it is possible to adopt the structure of a copolymer having the structure of both or either of the thermoplastic resin and elastomer component or a copolymer having an epoxy group, carbonyl group, halogen group, amine group, oxazoline group, hydroxy group, etc. able to react with the thermoplastic resin or elastomer component. These may be selected depending upon the type of the thermoplastic resin and elastomer component to be mixed, but examples of the usually used ones are styrene/ethylene-butylene block copolymers (SEBS) and their maleic acid-modified products, EPDM, EPM, EPDM/styrene or EPDM/acrylonitrile graft copolymers and their maleic acid-modified products, styrene/maleate copolymers, reactive phenoxine, etc. The amount of the compatibilizer blended in is not particularly limited, but preferably is 0.5 to 10 parts by weight per 100 parts by weight of the polymer components (total of thermoplastic resin and elastomer components).

[0036] The ratio of the specific thermoplastic resin (A) and elastomer component (B) in the case of blending a thermoplastic resin and elastomer is not particularly limited, but may be suitably decided by the balance of the thickness of the film, resistance to air permeation, and pliability, but the preferable range is an (A)/(B) of 10/90 to 90/10, more preferably 10/80 to 85/15.

[0037] The polymer composition according to the present invention may have mixed in it, in addition to the above necessary polymer components, a compatibilizer polymer or other polymer to an extent not detracting from the necessary properties of the polymer composition for a tire according to the present invention. The purpose of mixing in other polymers may be to improve the compatibility of the thermoplastic resin and elastomer component, to improve the film-forming ability of the material, to improve the heat resistance, and to reduce costs. As materials used for this, for example, polyethylene (PE), polypropylene (PP), polystyrene (PS), ABS, SBS, polycarbonate (PC), etc. may be exemplified. The polymer composition according to the present invention may further include any agents generally mixed into a polymer formulation such as fillers (calcium carbonate, titanium oxide, alumina, etc.), carbon black, white carbon, and other reinforcers, softeners, plasticizers, processing adjuvants, pigments, dyes, antioxidants and vulcanization agents (cross-linking agents), vulcanization adjuvants (cross-linking adjuvants), etc. so long as not detracting from the above requirements of the air permeation coefficient and the Young's modulus.

[0038] The vulcanization agent, vulcanization adjuvant, vulcanization conditions (temperature, time), etc. in the case of dynamic vulcanization may be suitably determined depending upon the composition of the elastomer component added and are not particularly limited.

[0039] Examples of the vulcanization agent are a conventional rubber vulcanization agent (or cross-linking agent). Specifically, examples of a sulfur type vulcanization agent are powdered sulfur, precipitated sulfur, high dispersion sulfur, surface treated sulfur, insoluble sulfur, dimorpholine disulfide, alkylphenol disulfide, etc. For example, about 0.5

to 4 phr (parts by weight per 100 parts by weight of rubber component (or polymer)) may be used.

[0040] Further, examples of a vulcanization agent of the organic peroxide type are benzoyl peroxide, t-butylhydroperoxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethylhexane-2,5-di(peroxybenzoate), etc. For example, 1 to 15 phr or so may be used.

[0041] Further, examples of a vulcanization agent of the phenolic resin type are a bromide of an alkylphenol resin or a mixed cross-linking agent containing tin chloride, chloroprene, or other halogen donor and an alkylphenol resin. For example, 1 to 20 phr or so may be used.

[0042] In addition, zinc white (5 phr or so), magnesium oxide (4 phr or so), litharge (10 to 20 phr or so), p-quinone dioxime, p-dibenzoylquinone dioxime, tetrachloro-p-benzoquinone, poly-p-dinitrosobenzene (2 to 10 phr or so), and methylene dianiline (0.2 to 10 phr or so) may be used.

[0043] Further, a vulcanization accelerator may be optionally added. As a vulcanization accelerator, use may be made of aldehyde ammonia types, guanidine types, thiazole types, sulfenamide types, thiuram types, dithio carbonate types, thiourea types, and other general vulcanization accelerators in amounts of for example 0.5 to 2 phr.

[0044] Specifically, as an aldehyde ammonia type vulcanization accelerator, hexamethylene tetramine etc.;

as a guanidine type vulcanization accelerator, diphenyl guanidine etc.;

as a thiazole type vulcanization accelerator, dibenzothiazyl disulfide (DM), 2-mercaptobenzothiazole and its Zn salt, cyclohexylamine salt, etc.;

as a sulfenamide type vulcanization accelerator, cyclohexylbenzothiazylsulfenamide (CBS), N-oxydiethylenbenzothiazyl-2-sulfenamide, N-t-butyl-2-benzothiazolesulfenamide, 2-(thymolpolynyldithio) benzothiazole, etc.;

as a thiuram type vulcanization accelerator, tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide, tetramethylthiuram monosulfide (TMTM), dipentamethylenethiuram tetrasulfide, etc.;

as a dithio acid salt type vulcanization accelerator, a Zn-dimethyldithiocarbamate, Zn-diethyldithiocarbamate, Zn-di-n-butylthiocarbamate, Zn-ethylphenyldithiocarbamate, Te-diethyldithiocarbamate, Cu-dimethyldithiocarbamate, Fe-dimethyldithiocarbamate, pipercolinepipercolyldithiocarbamate, etc.; and

as a thiourea type vulcanization accelerator, ethylene thiourea, diethyl thiourea, etc. have been disclosed.

[0045] Further, examples of a vulcanization acceleration adjuvant are a general rubber adjuvant together. For example, zinc white (5 phr or so), stearic acid or oleic acid and Zn salts of the same (2 to 4 phr or so), etc. may be used.

[0046] The pneumatic tire according to a first aspect of the present invention and the method of production of the same will now be explained in further detail.

[0047] The air permeation preventive layer of the pneumatic tire according to the present invention may be arranged at any position inside the tire, that is, at the inside or outside of the carcass layer or at another position. The point is that the object of the present invention be achieved by arranging it so as to prevent the permeation and diffusion of air from the inside of the tire and enable the long term retention of the air pressure inside the tire.

[0048] Figure 4 is a semi-sectional view in the meridial direction showing a typical example of the arrangement of the air permeation preventive layer of the pneumatic tire. In Fig. 4, a carcass layer 10 bridges a pair of left and right bead cores 9, 9. The air permeation preventive layer 11 is provided at the inner surface of the tire at the inside of the carcass layer 10. This air permeation preventive layer 11 is comprised of a cylindrical thermoplastic film in the first aspect of the present invention. In Fig. 4, 12 denotes a side wall.

[0049] Explaining the method of manufacturing a pneumatic tire having an air permeation preventive layer comprised of a cylindrical thermoplastic film according to the first aspect of the present invention taking as an example the case of arranging the air permeation preventive layer 11 at the inside of the carcass layer 10 as shown in Fig. 4, either one or more types of a thermoplastic resin having an action of preventing air permeation are fabricated into a single or multiple layers of cylindrical thermoplastic film by conventional extrusion, for example, inflation molding.

[0050] Next, the extruded single or multiple layers of cylindrical thermoplastic film are fit over the drum for molding the tire at the time of molding the green tire by cutting and supplying the necessary amount on the drum. This cylindrical thermoplastic film may be wound up once on a roll etc. and supplied on the molding drum at the time of molding the green tire.

[0051] Note that, instead of extruding the film into a cylinder, it is also possible to join the ends of strips of film and fuse them to make a cylindrical film.

[0052] On the cylindrical thermoplastic film fit over the molding drum are laid the carcass, sides, belt, tread, and rest of the tire members. This laminate is inflated as usual to produce the green tire which can then be vulcanized and made integral to produce a pneumatic tire.

[0053] The material of the rubber layer to which the air permeation preventive layer is laminated according to the present invention is not particularly limited. Any rubber material which has been generally used in the past as a rubber material for tires may be used. Examples of such a rubber, are a rubber composition comprising NR, IR, BR, SBR, or another diene rubber, a halogenated butyl rubber, an ethylene-propylene copolymer rubber, a styrene elastomer, etc.

to which carbon black, process oil, vulcanizers, and other additives have been added.

[0054] The cylindrical thermoplastic resin film of the present invention used may be a single layer or may be a multiple layer film obtained by providing a polyolefin, aliphatic polyamide, or urethane type resin adhesive layer on the two surfaces of the film of the above air permeation preventive resin as described in Japanese Unexamined Patent Publication (Kokai) No. 6-40207 mentioned above or further may be a film obtained by dispersing into a matrix of another thermoplastic resin a flat oriented polymer comprised of a single non-air permeable thermoplastic resins as described in Japanese Patent Application No. 7-55929 filed March 15, 1995 by the same applicant.

[0055] Further, it is possible to include any elastomer component to keep these thermoplastic resins pliable and to use as a film the blend of Japanese Patent Application No. 7-8394 filed on January 23, 1995 by the same applicant which uses the elastomer component as the domain and the resin layer as the matrix.

[0056] In the present invention, by using a single or multiple layer cylindrical film formed by inflation etc., as mentioned above, it is possible to prevent the tire from elongating nonuniformly at the time of inflation and deteriorating in uniformity since the difference in modulus between the splice portions (in the end the film becomes double layered) and other portions becomes large due to the presence of the splice portions (portions where film is joined). Looking at the difference in modulus, in the case of, for example, a butyl rubber liner, the difference between the splice portions (Young's modulus of about 10 MPa) and the nonsplice portions (Young's modulus of about 5 MPa/cm²) is a relatively small 5 MPa, but, for example, in the case of a resin film of a blend of nylon 6 resin and olefinic resin (weight ratio of 60/40), the difference between the splice portions (about 400 MPa) and the nonsplice portions (about 200 MPa) is 200 MPa.

[0057] Further, when using a cylindrical film as the air permeation preventive layer, as in the present invention, the film is just fit over the molding drum when molding the tire, and therefore, the work is extremely easy, while wrapping the film and adhering the connecting portions as in the past is poor in work efficiency and further there is the chance of a problem occurring of poor connection. Alternatively, if wrinkles occur in the splice portions, air will leak out through them and the desired goal will not be able to be achieved.

[0058] According to the second aspect of the present invention, there is provided a pneumatic tire having a plurality of air permeation preventive layers covering the inner surface of the tire substantially in the circumferential direction of the tire continuously at least two turns and each comprised of a film of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and elastomer having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa.

[0059] According to the second aspect of the present invention, further, there is provided a pneumatic tire having a plurality of air permeation preventive layers substantially covering the inner surface of the tire and each comprised of a film of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and elastomer having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa and arranged in such a manner that the splice portions of the film do not coincide at the same location on the circumference of the tire.

[0060] According to the second aspect of the present invention, as shown in Fig. 5, the method of arrangement of the polymer film 13, covering the inner surface of the tire substantially in the circumferential direction of the tire continuously at least two turns and comprised of a film of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and elastomer with an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa, is not particularly limited. An endless number may be considered. For example, as shown in Fig. 5(A-1) (sectional view) and (A-2) (sectional view), there are overall at least two polymer films 13 at the inner circumference of the tire.

[0061] Further, regarding the method of splicing, the tire shown in Fig. 5(B-1) is an example where the polymer film 13 covers the inner surface of the tire continuously by at least two turns in the circumferential direction of the tire and there is a single splice portion X. Further, the tire shown in Fig. 5(B-2) (side view) is an example where two polymer films 13 are arranged so that the splice portion Y and splice portion Z do not coincide at the same location on the tire circumference. Note that the two or more polymer films may be the same material or different. Further, the polymer film may be adhered or bonded after molding in accordance with a conventional method or may be coated in accordance with a conventional method. Further, the plurality of films do not have to be adjacent unless at the outermost layer. For example, there is no problem if there is a carcass layer etc. between them.

[0062] Further, according to the present invention, it is preferable that the amount of step S (mm) of the splice portion shown in Fig. 6 and the circumferential length L (mm) at the crown center portion be:

$$-0.05 \leq S/L \leq 0.05$$

[0063] Outside this range, there is a tendency for the uniformity to deteriorate. Note that in the case of Fig. (6-a), S is made larger than 0, while in the case of Fig. (6-b), S is made smaller than 0.

[0064] Further, according to the present invention, as shown in Fig. 7, a number of layers of polymer film 15 arranged at the inside of the carcass layer 14 are provided, and therefore, the stress will not concentrate at just the splice portion 16 even if lift is caused at the time of the second molding process, and therefore, no peeling (splice opening) of the splice portion 16 will occur even if there is elongation in the direction due to lift.

[0065] According to the third aspect of the present invention, there is provided a pneumatic tire of a single-ply carcass construction using, as an air permeation preventive layer, a film of a thermoplastic elastomer composition comprised of a thermoplastic resin or a blend of a thermoplastic resin component and elastomer component having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg, concentrating the splice portions of the carcass layer and air permeation preventive layer at substantially one location on the circumference during the molding, and making the amount of splice between the carcass and air permeation preventive layer 5 to 60 mm.

[0066] In the pneumatic tire of the single-ply carcass construction according to the third aspect of the present invention, for example, as shown in Figs. 8 to 11, the carcass 17 and a film of a thermoplastic elastomer composition comprised of a thermoplastic resin or a blend thereof with an elastomer are used in a pre-adhered state and the amount of overlap of the splice portion 19 at the time of molding is made 5 to 60 mm, preferably 10 to 50 mm. In this manner, according to the present invention, since the step difference at the splice portion 19 is small, it is possible to increase the amount of splice as explained above, whereby it becomes possible to obtain a sufficient splice strength without causing a deterioration of the uniformity.

[0067] In a second embodiment of the third aspect of the present invention, the overlap portion of the splice is coated with a tackifier to increase the bond strength of the splice portion and reduce the amount of splice from the case of no coating of a tackifier and enable the amount of overlap of the splice to be made 3 to 60 mm, preferably 3 to 50 mm. Note that the tackifier coated on the splice portion is not particularly limited. Any tackifier conventionally used in the past may be used by dissolving it in a solvent and coating it to a thickness of for example 1 μ m to 100 μ m. More specifically, for example, (a) a rosin resin (gum rosin, tall oil rosin, wood rosin, and other rosins; hydrated rosin, unhomogenized rosin, polymerized rosin, malcata rosin, and other basic rosins; rosin glycerine ester (ester gum), hydrated rosin-glycerine ester, and other rosin esters; and (b) terpene phenol resins and other resins having polar groups, resins not having polar groups, for example, α -pinene-based, β -pinene-based, dipentene-based (limonen), and other terpene resins; and aromatic hydrocarbon modified terpenes and other natural substances and their derivatives and for example (c) aliphatic, alicyclic, aromatic, and other petroleum resins; (d) cumarin-indene resins; (e) styrene type, substituted styrene type, and other styrene type resins and other polymer type resins or for example (f) alkylphenol resins, rosin-modified phenol resins, and other phenol type resins; and (g) xylene resins and other condensed resins. These may be used dissolved or suspended in a solvent in accordance with need. As such a solvent, use may be made of a general solvent. As specific examples, mention may be made of aromatic solvents (benzene, toluene, xylene, etc.), aromatic and aliphatic mixtures (M.S.P., S.B.P., Swazol 100, Swazol 200, Benzolallo 40, H.A.W.S., White Spirit, etc.), aliphatic esters (rubber volatile oil, ethyl acetate, etc.), alcohol ketone (methanol, acetone, methylethylketone, methylisobutylketone), etc. may be exemplified. It is possible to select the specific solvent among these solvents depending upon the rate of evaporation. These solvents may be used as mixtures of two or more types. The amount of the solvent added should be determined depending upon the viscosity of the tackifier. The viscosity is 10 cps to 1000 cps, preferably 50 to 500 cps. Further, the above resin and thermoplastic resin or thermoplastic elastomer composition may be mixed and used for the overlap portion in the state generally called a "hot melt". The thickness at this time is 1 μ m to 100 μ m. Further, a polyester polyol/isocyanate type tackifier or acrylic acid ester copolymer/organic peroxide type tackifier may be suitably used. For example, as the polyester polyol/isocyanate type tackifier used in the present invention, the following may be exemplified.

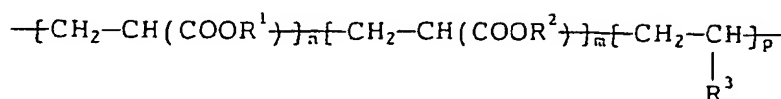
[0068] That is, as the polyester polyol, there are for example a condensed polyester polyol, lactone-type polyester polyol, polycarbonate diol, etc., but in general a condensed polyester polyol is often used. More specifically, there are ones obtained by a dehydrogenation condensation reaction of adipic acid and glycol and triol such as ethylene adipate, butylene adipate, diethylene adipate, etc. The molecular weight is preferably 3000 or more. If the molecular weight is less than 3000, there is a tendency for the tackiness to be insufficient. A polyester polyol is selected giving a critical surface tension difference γ_c between the rubber component and film component of the tire of not more than 3.

[0069] Examples of the isocyanate component usable as the cross-linking agent are those which are cross-linked by the heat at the time of vulcanization of the tire. Specific examples are TDI, MDI, crude MDI, NDI, HDI, IPDI, etc. The ratio of mixture of the polyester polyol and the isocyanate is preferably in the range of an index, $(\text{-NCO/-OH} \times 100 =)$ of 50 to 200. Outside of this range, there is poor tackiness, the bondability declines, and the tire members and thermoplastic film are no longer joined.

[0070] Catalysts, antioxidants, coloring agents, etc. generally used for urethane may also be suitably mixed in. Further, the above-mentioned tackifiers and solvents may also be used.

[0071] Examples of the acrylic acid ester copolymer/organic peroxide tackifier used in the present invention are, for example, of an acrylic acid ester copolymer (for example, polymers obtained by polymerizing butyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, and other monomers and copolymers with ethylene etc.) These are generally used as tackifiers

before cross-linking by the organic peroxide. The polymer has a Tg of 40°C or less, has tackiness, and typically is represented by the following general formula:



wherein, R¹ and R² are substituent groups selected from C₁₂ or less alkyl groups, arakyl groups, and aryl groups, R³ is hydrogen or a C₅ or less alkyl group, n and m are integers of 1 or more, and p is 0 or an integer of 1 or more. Examples of the cross-linking agent of the acrylic acid ester copolymer are a general organic peroxide. For example, mention may be made of benzoyl peroxide, t-butylhydroperoxide, 2,4-dichloro dibenzoyl peroxide, 2,5-dimethyl-2,4 di (t-butyl peroxide)hexane, 2,5-dimethyl hexane-2,5-di(peroxybenzoate), etc. in an amount of 1 to 15 parts by weight per 100 parts of the acrylic acid ester copolymer.

[0072] In addition, the above coloring agents, antioxidants, tackifiers, solvents, etc. may be mixed in. The air permeation preventive layer 18 for preventing air leakage may be arranged at the outside of the carcass layer 17 as shown in Fig. 9. Further, it may be arranged at the inside of the carcass layer as shown in Figs. 10 and 11.

[0073] The pneumatic tire according to the third aspect of the present invention may be produced by conventional methods except for using the above-mentioned specific film as the air permeation preventive layer, the splice portions of the carcass and air permeation preventive layer is concentrated at a single location, and the amount of the splice is made 5 to 60 mm.

[0074] The pneumatic tire according to the fourth aspect of the present invention can give a pneumatic tire having a good uniformity since it uses, as an air permeation preventive layer, the above specific film, wraps the air permeation preventive layer at least once around the drum for molding the green tire and joins it, then wraps a carcass layer on the circumference of the tire from a position 5 to 50 cm away so that the stress will not easily concentrate at the splice of the air permeation preventive layer, the splice portion will not open, and portions of a high rigidity will not concentrate at the circumferential direction. At this time, the material may be fed after preadhering the air permeation preventive layer and the carcass layer offset in the direction of wrapping on the molding drum. Further, the above-mentioned tackifier may be coated at the splice portions of the air permeation preventive layers or on the entire surface.

EXAMPLES

[0075] The present invention will now be explained in further detail by Examples and Comparative Examples, but of course the scope of the present invention is not limited to these Examples.

Example I-1

[0076] A three-layer film comprised of two polypropylene resin layers (thickness of 0.02 mm each) between which is laminated a polyvinylidene chloride resin layer (thickness of 0.05 mm) was processed into a cylindrical film of a diameter of 345 mm and a thickness of 0.09 mm by a multilayer inflation device having two general 40 mmφ resin extruders and then wound up. A 360 mm length was cut out from the wound up cylindrical film and fit over the tire molding drum. On the cylindrical film were laid the carcass, sides, belt, tread, and other tire members. This assembly was then inflated to fabricate a green tire.

[0077] Here, as the polyvinylidene chloride, Dow Chemical F-313 was used and as the polypropylene resin Tokuyama PER R110E was used.

[0078] Next, the green tire was vulcanized at 185°C for 15 minutes at a pressure of 2.3 MPa to finish a tire of the tire size 165SR13.

[0079] The time for setting the cylindrical film on the molding drum at the time of formation of the green tire, the uniformity of the produced pneumatic tire, and the air leakage of the resultant tires were measured. The results are shown in Table I-1.

Test Method for Uniformity

[0080] The uniformity was represented by the RFV value according to JASO C607-87 "Test Method of Uniformity of Automobile Tires".

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Test Method for Tire Air Leakage

[0081] A 165SR13 steel radial tire (rim: 13 × 41/2-J) was used and allowed to stand for three months under conditions of an initial pressure of 200 kPa, no load, and a room temperature of 21°C. The pressure was measured every 4 days.

[0082] The value α was found by regression to the following formula:

$$P_t/P_o = \exp(-\alpha t)$$

where P_t is the measurement pressure, P_o is the initial pressure, and t is the number of elapsed days. The obtained value α is used and $t = 30$ (days) inserted to obtain:

$$\beta = [1 - \exp(-\alpha t)] \times 100$$

The value β is made the rate of pressure loss (%/month) per month.

Comparative Example I-1

[0083] The same three-layer film as that prepared in Example I-1 cut out to a strip of a width of 360 mm and a thickness of 0.09 mm was wrapped around the tire molding drum. The splice portions were bonded by a usually used phenol resin adhesive, then a tire was fabricated in the same way as in Example I-1. The resultant tire was subjected to the same tests as Example I-1. Further, the liner wrapping process time was the time for wrapping the strip-like film, joining the splice portion by an adhesive, and setting the result over the molding drum at the time of forming the green tire. The results are shown in Table I-1.

Table I-1

	Shape of liner	Liner wrapping process time*1	Uniformity*2	Tire air leakage
Ex. I-1	Cylindrical, no splice	70	93	100
Comp. Ex. I-1	Strip-like film joined, splice	100	100	100

*1: Processing time when using processing time of Comparative Example I-1 100 (index).

*2: Average RFV value of $n = 20$ expressed as index.

Examples I-2 and I-3

[0084] The formulations shown in Table I-2, that is, the rubber material and the cross-linking compounding agent required for the dynamic cross-linking, were mixed by a biaxial kneader/extruder and extruded into strands. These were cooled, then pelletized by a resin pelletizer, then melt-extruded/inflation molded using a usual 40 mm monoaxial resin extruder to fabricate cylindrical films.

[0085] Note that the resin material was a cross-linked thermoplastic resin material with a resin layer as a matrix and a rubber layer as a domain (dispersed layer).

[0086] Next, tires were fabricated in the same way as in Example I-1 and used for the tests. The results are shown in Table I-3.

Table I-2

	Ex. I-2	Ex. I-3
N6*1	50	
MXD6*2		50
Br-IPMS*3	50	50

*1: Amilan CM1041, made by Toray.

*2: Reny 6002, made by Mitsubishi Gas Chemical.

*3: Bromide of paramethylstyrene-isobutylene copolymer, XP-50, 90-10, made by Exxon Chemical.

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Table I-2 (continued)

	Ex. I-2	Ex. I-3
GPF ^{*4}	30	30
Paraffinic process oil	10	10
Zinc white	0.25	0.25
Stearic acid	1	1
Zinc stearate	0.5	0.5

*4: Carbon black, Sheast V, made by Tokai Carbon.

Table I-3

	Shape of liner	Liner wrapping process time ^{*1}	Uniformity ^{*2}	Action preventing air permeation ^{*3}
Ex. I-2	Cylindrical, no splice	70	90	100
Ex. I-3	Cylindrical, no splice	71	90	100
Comp. Ex. I-1	Strips joined, splice	100	100	100

*1: Processing time when using processing time of Comparative Example 1-1 100 (index).

*2: Average RFV value of n = 20 expressed as index.

*3: Shows measured value of air pressure measured by tire air leakage performance test.

Examples II-1 to II-9 and Comparative Examples II-1 to II-5

[0087] As shown in Table II-1, polymer films comprised of the materials A to D were used to fabricate tires having the air permeation preventive layers of the configurations shown in Table I (size: 165SR13, rim size: 13 × 41/2-J). These tires and the Standard Examples II-1 and II-2 were tested as follows:

[0088] The results are shown in Table II-1.

Test Method for Air Deposit

[0089] Vulcanized tires were cut. Those where problems with air deposits were observed were ranked as "defective" (x) and those where they were not observed were ranked as "good" (o).

Test Method for Moldability

[0090] Tires where the materials ended up elongating at the time of molding were ranked as "defective" (x) and those where they did not elongate were ranked as "good" (o).

Test Method for Splice Opening

[0091] Vulcanized tires with splice portions of the air permeation preventive layer opened up were ranked as "defective" (x) and those where they did not open up were ranked as "good" (o).

Test Method for Uniformity

[0092] The RFV was measured in accordance with JASO C-607-87 (Test Method of Uniformity of Automobile Tires). The results were indicated indexed to the inverse of the measured value of Standard Example II-2, a typical conventional tire, as 100 (the larger the figure, the better).

Test Method for Air Leakage (Rate of Pressure Loss)

[0093] As explained above.

Table II-1

	Standard Ex. II-1	Standard Ex. II-2	Ex. II-1	Ex. II-2	Ex. II-3	Ex. II-4	Ex. II-5	Ex. II-6	Ex. II-7	Ex. II-8	Ex. II-9
Material	A	D	A	B	C	A	A	A	A	A	A
Method of splicing air permeation preventive layer	1 layer	1 layer	2 layers B-1	2 layers B-1	2 layers B-1	3 layers B-1	2 layers B-1	6 layers B-1	2 layers B-1	2 layers B-1	2 layers B-2
Gauge t per layer of air permeation preventive layer (mm)	0.02	0.5	0.02	0.02	0.02	0.02	0.2	0.2	0.02	0.02	0.02
Total gauge t of air permeation preventive layer (mm)	0.02	0.5	0.04	0.04	0.04	0.06	0.4	1.2	0.04	0.04	0.04
Splice amount S/circumferential length L	+0.003	+0.002	+0.003	+0.003	+0.003	+0.003	+0.003	+0.003	-0.05	+0.05	+0.003 (both locations)
Air deposit	o	o	o	o	o	o	o	o	o	o	o
Moldability	o	o	o	o	o	o	o	o	o	o	o
Splice opening	x	o	o	o	o	o	o	o	o	o	o
Uniformity (index)	103	100	112	112	111	120	111	125	104	106	112
Rate of pressure loss (%/month)	3	2.7	1.8	0.8	0.6	1.3	0.2	0.1	1.8	1.8	1.8
Tire mass (kg)	6.36	7.0	6.38	6.38	6.38	6.39	6.57	7.0	6.38	6.38	6.38
Remarks	1 air permeation prevention layer	Tie rubber gauge 0.7 mm									

Table II-1 (Continued)

	Standard Ex. II-1	Standard Ex. II-2	Comp. Ex. II-1	Comp. Ex. II-2	Comp. Ex. II-3	Comp. Ex. II-4	Comp. Ex. II-5
Material	A	D	A	A	A	A	A
Method of splicing air permeation preventive layer	1 layer	1 layer	2 layers B-1	2 layers B-1	7 layers B-1	2 layers B-1	2 layers B-1
Gauge t per layer of air permeation preventive layer (mm)	0.02	0.5	0.01	0.3	0.2	0.02	0.02
Total gauge t of air permeation preventive layer (mm)	0.02	0.5	0.02	0.6	1.4	0.04	0.04
Splice amount S/circumferential length L	+0.003	+0.002	+0.003	+0.003	+0.003	-0.1	+0.1
Air deposit	o	o	o	x	o	o	o
Moldability	o	o	x	o	o	o	o
Splice opening	x	o	o	o	o	o	o
Uniformity (index)	103	100	116	110	125	83	78
Rate of pressure loss (Z/month)	3	2.7	3	0.1	0.06	1.8	1.8
Tire mass (kg)	6.36	7.0	6.36	6.68	7.11	6.38	6.38
Remarks	1 air permeation preventive layer	Tie rubber gauge 0.7 mm	Thin gauge per layer	Thick gauge per layer	Thick total gauge	S/L small	S/L large

Footnote of Table I (All Parts are Parts by Weight)

[0094] Material A: Material comprised of 28 parts of nylon 6 (N6) (CM4061 made by Toray), 4.2 parts of nylon MXD6 (MXD6) (Reny 6002 made by Mitsubishi Gas Chemical), 30 parts of maleic acid-modified ethylene-propylene rubber (M-EPM), and 0.18 part of methylene dianiline having an air permeation coefficient of 2.13×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 257 MPa.

[0095] Material B: Material comprised of 25.2 parts of nylon 6 (N6), 37.8 parts of MXD6, 48.9 parts of Master Batch A (100 parts of butyl rubber bromide: Exxon Bromobutyl 2244 made by Exxon Chemical, 60 parts of carbon black GPF: Sheast V made by Tokai Carbon, 1 part of stearic acid, 10 parts of petroleum hydrocarbon resin: Escolet 1102 made by Esso, and 10 parts of paraffin process oil), 10 parts of Hizex Million 240M (EEA) made by Mitsui Petrochemical, 1.5 part of zinc white, 0.5 part of DM, and 0.3 part of sulfur having an air permeation coefficient of 0.84×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 244 MPa.

[0096] Material C: Material comprised of 25.2 parts of N6, 37.8 parts of MXD6, 27.0 parts of Br-(polyisobutylene-p-methylstyrene) (EXXPRO 89-4 made by Exxon Chemical), and 10 parts of nylon 6/nylon 66/nylon 610 (CM4001 made by Toray) having an air permeation coefficient of 0.63×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 317 MPa.

[0097] Material D: Butyl rubber (air permeation coefficient of 55×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 15 MPa)

Standard Example III-1, Examples III-1 to III-7, and Comparative Examples III-1 to III-5

[0098] As shown in Table III-1, the compositions, thicknesses, amount of splice overlap, and splice structure of the air permeation preventive layer were changed in various ways and tested (tire size: 165SR13). Note that the test methods were as follows:

Amount of Splice Overlap of Carcass and Inner Liner

[0099] The amount of overlap of the splice was the amount of overlap L at the time of molding of the carcass.

Test Method for Air Deposits

[0100] As explained above.

Splice Opening Due to Lift at Time of Molding

[0101] Vulcanized tires with splice portions of the air permeation preventive layer opening due to the lift at the time of molding were ranked as "defective" (x) and those not opening as "good" (o).

Test Method for Uniformity

[0102] The RFV was measured in accordance with JASO C-607-87 (Test Method of Uniformity of Automobile Tires) (n=10). The results were indicated indexed to the measured value of Standard Example III-1, a conventional tire, as 100. The larger the value, the better the uniformity.

Test Method for Air Leakage (Rate of Pressure Loss)

[0103] As explained above.

Productivity

[0104] The minimum necessary number of rotations of the molding drum at the time of the first green molding of the carcass and inner liner (and tie rubber):

o: Can be molded by one turn of the molding drum

x: Requires at least 2 turns of the molding drum

Air Permeation Preventive Materials Used in Table III-1(1) Production of Polybutylene Terephthalate

[0105] 1,4 butane diol and dimethyl terephthalate were mixed at a ratio by weight of 2/3 and reacted at 180°C. At that time, as the catalyst, use was made of tetraoctyl titanate. The reaction was stopped at the time when a stoichiometric amount of methanol was produced from this reaction and the result used as the polybutylene terephthalate.

(2) Production of Polypropylene Diimidosic Acid

[0106] Polypropylene amine and anhydrous trimellitic acid were reacted at ordinary temperature for 1.5 hours, then further reacted at 100°C for 3 hours under reduced pressure to prepare polypropylene diimido diacid.

(3) Preparation of Thermoplastic Polyester Elastomer (Material E)

[0107] 45 wt% of the above polybutylene terephthalate and 55 wt% of polypropylene diimido diacid were mixed and reacted at 250°C to prepare a thermoplastic polyester elastomer.

[0108] The thermoplastic polyester elastomer prepared by the above method was pelletized by a pelletizer, then some of the additives in Table III-2 were mixed in. This was extruded into a film using a resin extruder to produce a film of a width of 350 mm and thickness of 0.1 mm. The air permeation coefficient was 24.0×10^{-12} cc-cm/cm²-sec-cmHg and the Young's modulus was 180 MPa.

[0109] Material F-1: A material comprised of a thermoplastic resin component of 28 parts of nylon 6 (N6) (CM4061 made by Toray) and 42 parts of nylon MXD6 (MXD6) (Reny 6002 made by Mitsubishi Gas Chemical) and an elastomer component of 30 parts of maleic acid modified ethylene propylene rubber (M-EPM) and 0.18 part of methylene dianiline having an air permeation coefficient of 2.13×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 257 MPa.

[0110] Material F-2: A material comprised of a thermoplastic resin component of 25.2 parts of N6 and 37.8 parts of MXD6, an elastomer component of 48.9 parts of a master batch (100 parts of butyl rubber bromide: Exxon Bromobutyl 2244 made by Exxon Chemical, 60 parts of carbon black GPF: Sheast V made by Tokai Carbon, 1 part of stearic acid, 10 parts of petroleum hydrocarbon resin: Escolet 1102 made by Esso, and 10 parts of paraffin process oil), a compatibility component of 10 parts of Hizex Million 240M (EEA) made by Mitsui Petrochemical, and a dynamic vulcanization system of 1.5 part of zinc white, 0.5 part of DM, and 0.3 part of sulfur having an air permeation coefficient of 0.84×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 244 MPa.

[0111] Material F-3: A material comprised of a thermoplastic resin component of 25.2 parts of N6, 37.8 parts of MXD6 and 10 parts of nylon 6/nylon 66/nylon 610 (CM4001 made by Toray) and an elastomer component of 27.0 parts of Br-(polyisobutylene-p-methylstyrene) (EXXPRO 89-4 made by Exxon Chemical) having an air permeation coefficient of 0.63×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 317 MPa.

[0112] Butyl rubber: Br-ILR rubber composition (air permeation coefficient of 55×10^{-12} cc-cm/cm²-sec-cmHg and Young's modulus of 15 MPa)

Tackifier Used for Table III-1

[0113]

	Composition
EEA: ethylene ethyl acrylate copolymer DPDJ-6169 (Nihon Unika)	100
Quinton A-100 (Nihon Zeon)	60
Dicumyl peroxide	1
FEF-black	10
Toluene	400
MEK	100
n-hexane	100

[0114] In the above formulation, a kneader was used to mix the EEA, Quinton A-100, and FEF black. The result was then stirred by a homogenizer (8000 rpm) in a mixed solution of the toluene and subsequent components to make the tackifier. Finally, the dicumyl peroxide was added and the result stirred.

Table III-1

	Standard Ex. III-1	Comp. Ex. III-1	Comp. Ex. III-2	Comp. Ex. III-3	Comp. Ex. III-4	Comp. Ex. III-5
Air permeation preventive material ¹⁾	Butyl rubber	Butyl rubber	Butyl rubber	Butyl rubber	B-1	B-1
Air permeation coefficient $\times 10^{-12}$ (cc·cm/cm ² ·sec·cmHg)	55	55	55	55	2.13	2.13
Air permeation preventive layer gauge (mm)	0.50	0.50	0.50	0.10	0.10	0.10
Tie rubber gauge (mm)	0.70	0.70	none	none	none	none
Amount of overlap of molded splice of carcass and air permeation preventive layer (mm)	3 (carcass) 3 (liner)	3	3	3	3	65
Coating of tackifier	none	none	none	none	none	none
Structure of carcass splice	Fig. 3	Fig. 2	Fig. 8	Fig. 8	Fig. 8	Fig. 8
Rate of loss of air pressure (%/month)	2.7	2.7	2.7	5.1	Unevaluatable	0.7
Uniformity (index)	100	97	107	110		98
Rolling resistance (index)	100	100	94	97		101
Trouble due to air deposit of splice	0	x	0	0		0
Opening of splice due to lift at time of molding	0	0	0	0	x	0
Productivity	x	0	0	0	0	0
Weight (kg)	7.0	7.0	6.6	6.4	6.4	6.4
Remarks	-	-	With tie rubber is removed, rolling resistance increases	When butyl rubber is made thinner, air easily leaks	-	-

Table III-1 (Continued)

	Standard Ex. III-1	Ex. III-1	Ex. III-2	Ex. III-3	Ex. III-4	Ex. III-5	Ex. III-6	Ex. III-7	Ex. III-8
Air permeation preventive material ¹⁾	Butyl rubber	E	F-1	F-1	F-1	F-1	F-1	F-2	F-3
Air permeation coefficient $\times 10^{-12}$ (cc·cm/cm ² ·sec·cmHg)	55	24.0	2.13	2.13	2.13	2.13	2.13	0.84	0.63
Air permeation preventive layer gauge (mm)	0.50	0.3	0.10	0.10	0.10	0.10	0.10	0.05	0.05
Tie rubber gauge (mm)	0.70	none	none	none	none	none	none	none	none
Amount of overlap of molded splice of carcass and air permeation preventive layer (mm)	3 (carcass) 3 (liner)	10	5	10	50	60	3	10	10
Coating of tackifier	none	none	none	none	none	none	yes	none	none
Structure of carcass splice	Fig. 3	Fig. 8	Fig. 8	Fig. 8	Fig. 8	Fig. 8	Fig. 8	Fig. 8	Fig. 8
Rate of loss of air pressure (%/month)	2.7	2.1	0.7	0.7	0.7	0.7	0.7	0.6	0.5
Uniformity (index)	100	110	109	109	101	100	111	112	111
Rolling resistance (index)	100	102	102	102	101	101	102	102	102
Trouble due to air deposit of splice	o	o	o	o	o	o	o	o	o
Opening of splice due to lift at time of molding	o	o	o	o	o	o	o	o	o
Productivity	x	o	o	o	o	o	o	o	o
Weight (kg)	7.0	6.5	6.4	6.4	6.4	6.4	6.4	6.3	6.3
Remarks	-	-	-	-	-	-	If tackifier is used, amount of splice can be reduced.	-	-

Example IV-1 (Tire size 165SR13)

[0115] Sheet-like air permeation preventive layers obtained by cutting a three-layer film such as shown in Example I-1 were wrapped on a drum for molding green tires, the sheets were joined, then the carcass material was wrapped

from a position offset in the circumferential direction to obtain a pneumatic tire with a splice section as shown in Fig. 12. [0116] At this time, the experiments were run on a tire with an amount of the carcass splice of 5 mm, an amount of the splice of the air permeation preventive layer of 50 mm, and a distance between the carcass splice and the film splice portion in the circumferential direction of 20 cm.

[0117] As a result, since there is no carcass layer interposed between the splices of the air permeation preventive layer and the air permeation preventive layers are directly joined, those portions will not open up. Further, the only portion where the thickness of the joint portion of the carcass layer and air permeation preventive layer is large is the carcass splice portion, and therefore, a tire is obtained with a better uniformity than the conventional case of use of butyl rubber for the air permeation preventive layer (where thick portions are at both the carcass splice and rubber liner splice).

INDUSTRIAL APPLICABILITY

[0118] As explained above, according to the first aspect of the present invention, it becomes possible to lighten the weight of the tire without detracting from the retention of air pressure in the tire and, by using as the air permeation preventive layer a cylindrical thermoplastic film, it becomes possible to improve the quality and reliability of the pneumatic tire (that is, since there is no join of the film of the air permeation preventive layer, the elongation at the time of inflation in the tire molding process is constant and therefore the uniformity of the air permeation preventive layer is improved and, also, there is no liability of the join of the film opening up and causing a defective tire at the time of inflation) and possible to improve the efficiency of production of the pneumatic tire (work of adhering film being complicated, while insertion of cylindrical material inside green tire being easy).

[0119] Further, according to the second aspect of the present invention, by using, as the air permeation preventive layer, a film of a preferable thickness of 0.02 to 0.2 mm of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and elastomer with an air permeation preventive layer of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa and providing a plurality of layers at the inner circumferential surface of the tire as a whole, the effects are achieved of 1) a major reduction of weight becoming possible due to the gauge being extremely thin, 2) the suppression of air deposits at step differences as in the past, and therefore, the elimination of a case of trouble in vulcanization due to the gauge being extremely thin, and 3) a lack of deterioration of the moldability despite the thin gauge due to the high modulus.

[0120] Further, according to the third aspect of the present invention, by using, as the air permeation preventive layer, a film of a polymer composition containing a thermoplastic elastomer composition comprised of a thermoplastic resin or a blend of a thermoplastic resin and elastomer having an air permeation preventive layer of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg, molding the tire so that the splices of the carcass layer and air permeation preventive layer become substantially concentrated at a single location on the circumference, and the amount of the splice between the carcass and air permeation preventive layer is made 5 to 60 mm, it is possible to provide a lightweight pneumatic tire of a structure manufacturable with a good productivity without causing the deterioration of the rolling resistance, durability, etc.

[0121] Further, according to the fourth aspect of the present invention, by using, as an air permeation preventive film, a film of a polymer composition the same as that used in the above first to third aspects and arranging the splice portion of the layer at a position 5 to 50 cm away from the splice portion of the carcass layer on the circumference of the tire, it is possible to improve the uniformity compared with a conventional tire using a butyl rubber liner and prevent the splice portion of the air permeation preventive layer from opening up due to the lift at the time of vulcanization of the tire.

Claims

1. A pneumatic tire having at least one air permeation preventive layer comprised of a cylindrical film or sheet extruded, molded or heat-fused into a cylindrical shape and free from any connecting portion, composed of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and an elastomer component and having an air permeation coefficient of not more than 25×10^{-12} cc-cm/cm²-sec-cmHg and a Young's modulus of 1 to 500 MPa, wherein a plurality of air permeation preventive layers cover the inner surface of the tire by at least two continuous turns substantially in the tire circumferential direction.

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2. A pneumatic tire as claimed in claim 1, wherein the layers are arranged in such a manner that joints of a layer do not coincide at the same location on the tire circumference.
3. A pneumatic tire as claimed in claim 1 or 2, wherein the thickness of each layer is from 0.02 to 0.2.
4. A pneumatic tire as claimed in claim 1, wherein a tackifier is coated on the splice portion and the amount of splice is made 3 to 60 mm.
5. A pneumatic tire as claimed in claim 1, wherein the position of the splice of the air permeation preventive layer is separated from the position of the carcass splice and the air permeation preventive layer is brought into substantial direct contact with each other to form a cylindrical shape.

Fig. 1
(PRIOR ART)

FIG. 1 (a)

AFTER FIRST MOLDING STEP

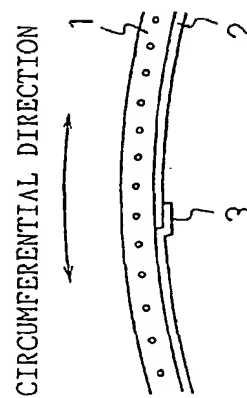


FIG. 1 (b)

AFTER SECOND MOLDING STEP

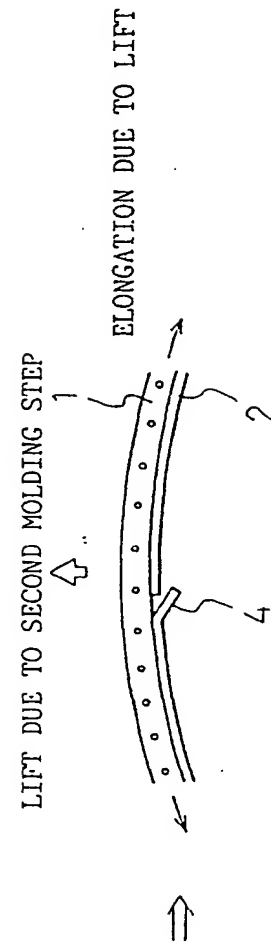


Fig.2

(PRIOR ART)

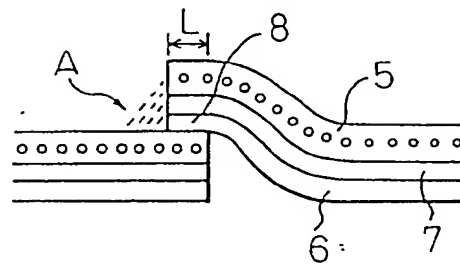


Fig.3

(PRIOR ART)

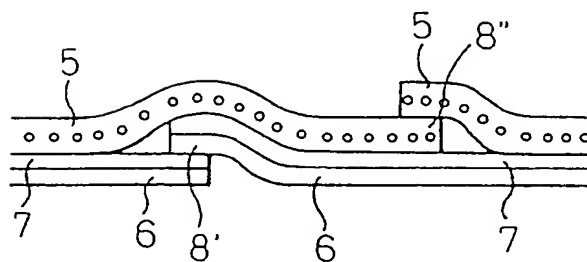


Fig.4

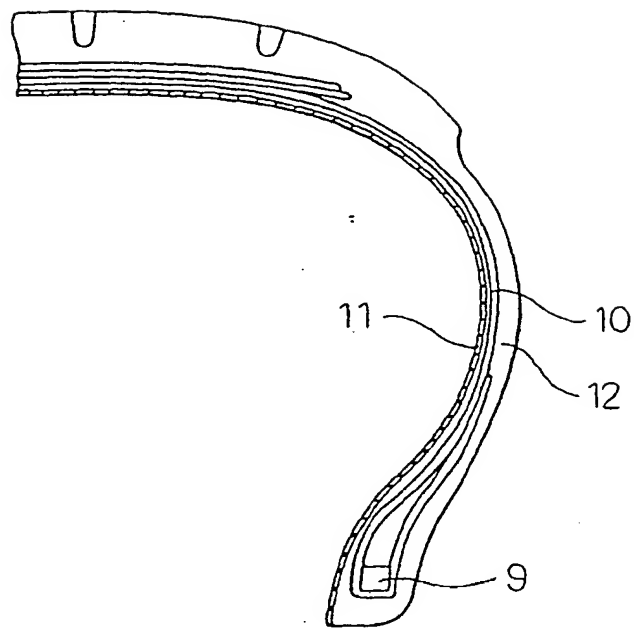


Fig. 5

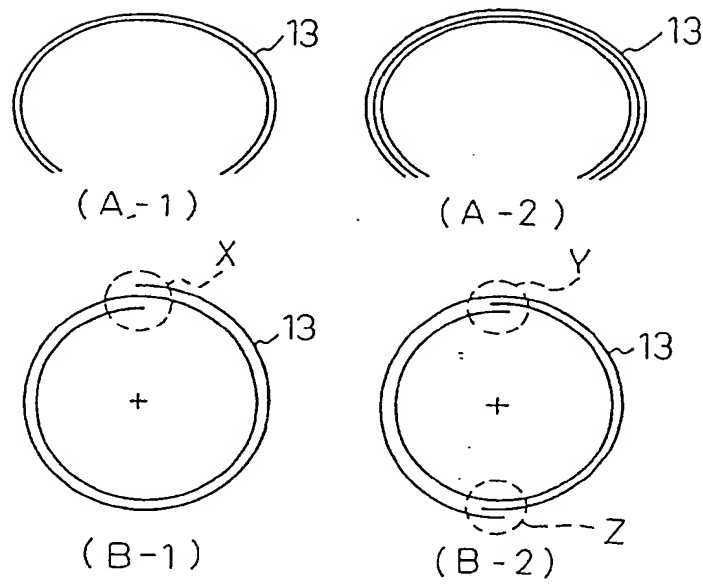


Fig. 6

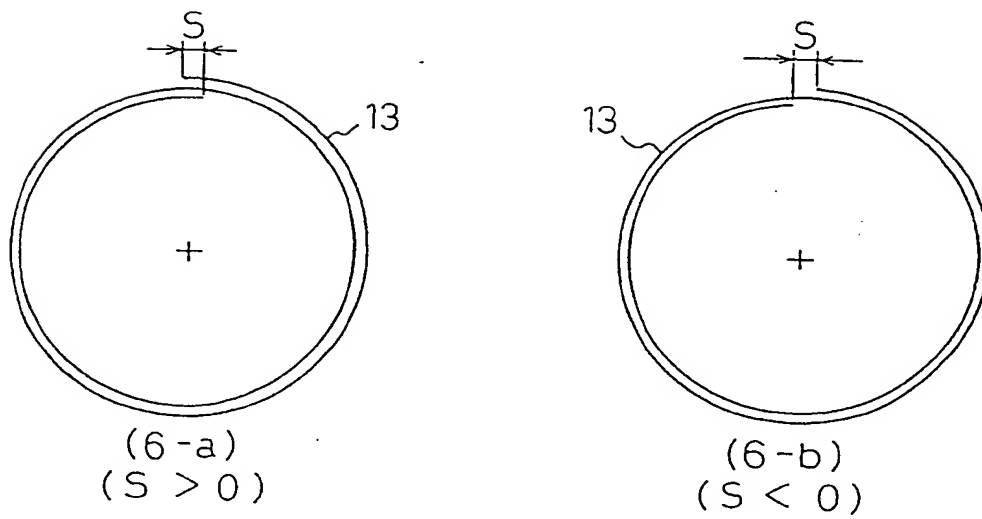


Fig.7

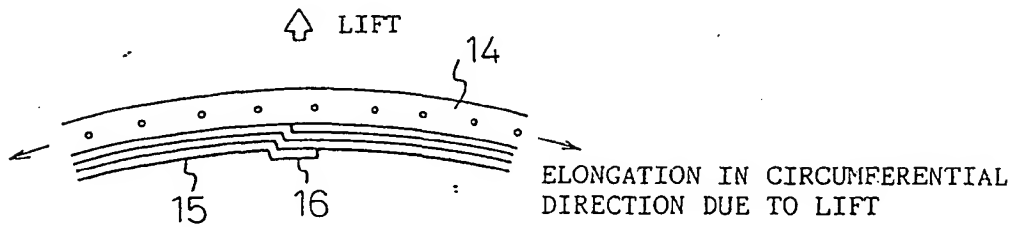


Fig.8

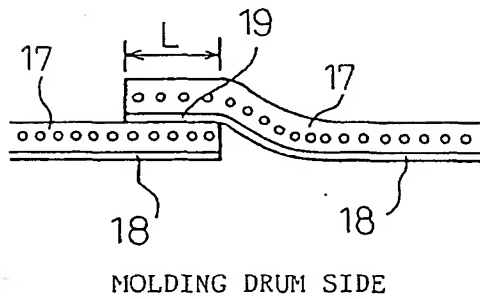


Fig.9

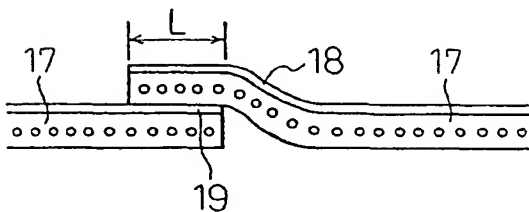


Fig.10

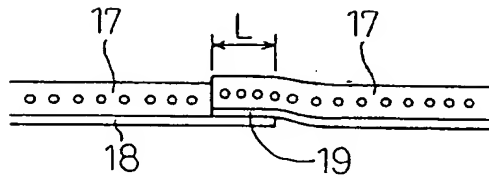


Fig.11

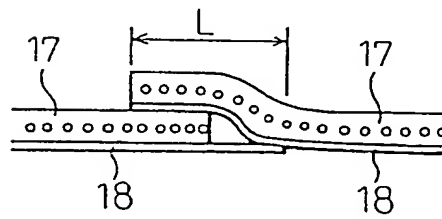
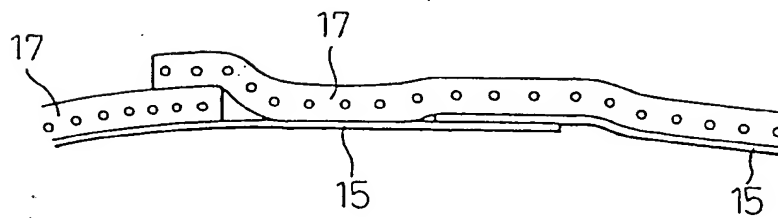
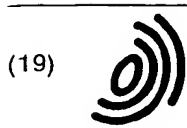


Fig.12



List of References

- 1 ... Carcass layer
- 2 ... Film liner (Polymer film)
- 3 ... Splice of film liner
- 4 ... Splice opening
- 5 ... Carcass
- 6 ... Inner liner layer (Air permeation preventive layer)
- 7 ... Tie rubber
- 8, 8', 8" ... Splice portions
- 9 ... Bead core
- 10 ... Carcass layer
- 11 ... Air permeation preventive layer
- 12 ... Side wall
- 13 ... Polymer film
- 14 ... Carcass layer
- 15 ... Polymer film
- 16 ... Splice portion
- 17 ... Carcass
- 18 ... Inner liner layer (Air permeation preventive layer)
- 19 ... Splice portion
- S ... Step amount
- X, Y, Z ... Splice portions



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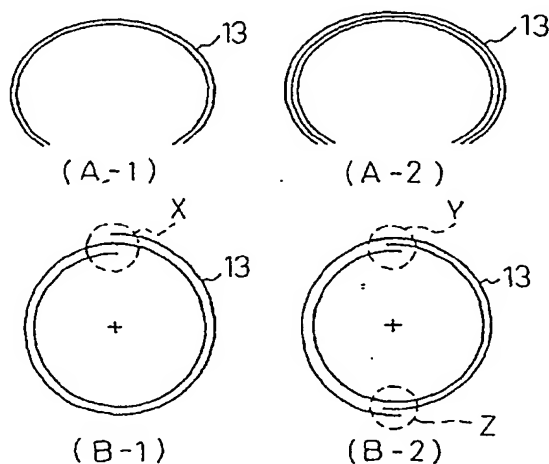
- Kaido, Hiroyuki, Yokohama Rubber Co., Ltd.
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- Yamakawa, Kazuto, Yokohama Rubber Co., Ltd.
Hiratsuka-shi, Kanagawa 254 (JP)
- Watanabe, Jiro, Yokohama Rubber Co., Ltd.
Hiratsuka-shi, Kanagawa 254 (JP)
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(54) Pneumatic tire

(57) A pneumatic tire having at least one air permeation preventive layer comprised of a cylindrical film or sheet extruded, molded or heat-fused into a cylindrical shape and free from any connecting portion, composed of a polymer composition containing a thermoplastic resin or a blend of a thermoplastic resin and an elastomer component and having an air permeation coefficient of not more than $25 \times 10^{-12} \text{cc-cm/cm}^2 \cdot \text{sec-cmHg}$ and a Young's modulus of 1 to 500MPa, wherein a plurality of air permeation preventive layers cover the inner surface of the tire by at least two continuous turns substantially in the tire circumferential direction.

Fig.5



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EUROPEAN SEARCH REPORT

Application Number
EP 01 11 5641

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	EP 0 337 279 A (HERCULES INC) 18 October 1989 (1989-10-18) * claim 1; examples *	1,3	B60C5/14 B60C1/00
Y	US 1 875 390 A (A. J. MUSSELMAN) 6 September 1932 (1932-09-06) * page 1, left-hand column, line 44 - line 50 *	1,3	
A	US 4 531 561 A (STUETTGEN FRIEDEL ET AL) 30 July 1985 (1985-07-30) * column 1, line 43 - line 50 *	1	
A	US 3 027 289 A (GITZINGER HARRY F) 27 March 1962 (1962-03-27) * column 6, line 53 - line 60 *	1	
A	US 4 928 741 A (RYE GROVER W ET AL) 29 May 1990 (1990-05-29)		
A	US 5 292 590 A (LIN KUANG F ET AL) 8 March 1994 (1994-03-08) * examples *		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B60C B29D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 June 2003	Examiner Baradat, J-L
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date O : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 5641

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05-06-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0337279	A	18-10-1989	AT	94477 T	15-10-1993
			AU	3261889 A	12-10-1989
			BR	8901717 A	21-11-1989
			CA	1331734 A1	30-08-1994
			DE	68909086 D1	21-10-1993
			DE	68909086 T2	13-01-1994
			EP	0337279 A2	18-10-1989
			ES	2042845 T3	16-12-1993
			JP	1314164 A	19-12-1989
			JP	2858780 B2	17-02-1999
			KR	9608294 B1	24-06-1996
			US	5040583 A	20-08-1991
			US	5156921 A	20-10-1992
			US	5292590 A	08-03-1994
US 1875390	A	06-09-1932	DE	558610 C	09-09-1932
			FR	715467 A	03-12-1931
			GB	368544 A	10-03-1932
			NL	30556 C	
			NL	56547 C	
US 4531561	A	30-07-1985	DE	2934936 A1	19-03-1981
			AT	1938 T	15-12-1982
			AU	540364 B2	15-11-1984
			AU	6178880 A	05-03-1981
			BR	8005466 A	10-03-1981
			CA	1144850 A1	19-04-1983
			DE	3061274 D1	13-01-1983
			EP	0026315 A1	08-04-1981
			ES	8104081 A1	01-07-1981
			IE	50049 B1	05-02-1986
			IL	60916 A	30-09-1982
			IN	154512 A1	03-11-1984
			JP	56075204 A	22-06-1981
			ZA	8005332 A	30-09-1981
US 3027289	A	27-03-1962	NONE		
US 4928741	A	29-05-1990	CA	1321279 A1	10-08-1993
US 5292590	A	08-03-1994	US	5040583 A	20-08-1991
			US	5156921 A	20-10-1992
			AT	94477 T	15-10-1993
			AU	3261889 A	12-10-1989
			BR	8901717 A	21-11-1989
			CA	1331734 A1	30-08-1994

EPO FORM P-459

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ON EUROPEAN PATENT APPLICATION NO.

EP 01 11 5641

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05-06-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5292590 A	DE	68909086 D1	21-10-1993
	DE	68909086 T2	13-01-1994
	EP	0337279 A2	18-10-1989
	ES	2042845 T3	16-12-1993
	JP	1314164 A	19-12-1989
	JP	2858780 B2	17-02-1999
	KR	9608294 B1	24-06-1996

EPD FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82